PHASE EVOLUTION IN DOPED POLYMER DERIVED SILICON OXYCARBIDE CERAMICS

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CERTIFICATE

This is certified that the work contained in the project entitled "Phase evolution in doped polymer derived silicon oxycarbide ceramics", carried out by Durga Prasad Rath (Roll No. 710CR1162) in partial fulfilment of the requirements of the award of Dual Degree in Ceramic Engineering at the National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other university/ institute for the award of any Degree or Diploma.

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Abstract

Polymer derived ceramics (PDC) is an important class of ceramics that are fabricated from the inert atmosphere pyrolysis of Si- containing precursors. Various Si- based ceramics including silicon oxycarbide (SiCO), silicon carbonitride (SiCN), silicon carbide (SiC), silicon borocarbonitride (SiBCN) etc. can be prepared from various Si- containing precursors. These ceramics are characterized by their high specific strength, oxidation resistance, enhanced creep resistance and other functional properties. One of the most important developments in the ceramic system is the possibility of using these materials as coatings for high temperature structural ceramics. Although oxidation resistance of PDCs are good, they need to be fabricated in the multilayer structures that includes phase stability with various other metal oxides and carbides. The present work focuses on transition metal modified Polymer derived ceramics (PDC). Poly (methyl) silsesquioxane was used as the preceramic polymer in the process. Various transition metal elements having similar atomic size and different valence such as Al and Ti were introduced in the SiCO structure to form modified PDC. The doping amount in the structure is varied to study effect of amount of transition metal doping at the molecular level on phase evolution at different temperatures Phase evolution and thermal behavior of the modified PDCs at different high temperatures are studied.

Keywords: PDC, Phase evolution, Transition metal doping, Oxidation resistance

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INTRODUCTION

1. INTRODUCTION

1.1 Polymer Derived Ceramics (PDC)

Preceramic polymers (polymers which are converted in to ceramics up on high temperature heat treatment), have been used for last four decades to produce so called Polymer Derived Ceramics (PDCs). The PDCs which have the most impact in the particular field are the ternary systems such as SiCO *[1]* and SiCN *[2]* as well as the quaternary system such as SiBCN *[3]*. The main advantage being the ease of shaping in the precursor stage by conventional method such as spinning, injection molding, blowing and resin transfer molding (RTM) and then converted in to ceramics by heat treatment above pyrolysis temperature *[4]*. The formation of wide range of ceramic materials predominantly depends on the modification of the polymers at the nano scale by addition of nano sized fillers or chemical additives, which eventually forms desired ceramic components up on heat treatment.

The PDCs route is a rapidly developing which has high potential in commercial development of pre ceramic polymers to produce ceramic shapes which was unprecedented. Moreover these are ceramic materials having excellent oxidation and creep resistance up to noticeably high temperature. The PDCs due to their extraordinary properties attract the attention in the structural ceramics field.

Applications of PDCs:

Due to their significant physical, chemical and functional properties along with the precursor level control PDCs are well recognized in the areas such as defense, information technology, energy sector along with environmental systems and biomedical components *[4]*.

Some tweaks in the preceramic material features lead to the formation of preceramic polymer derived fibers *[5] [6] [7]*. PDCs are used in the Ceramic Matrix Composites due to relatively cheap equipment and lower processing temperature along with the capability to produce very large and complex parts. High volume porosity material can be processed by the polymeric route using the preceramic polymers which are generally god in producing porous materials having porosity in the range of nano meters to a few millimeters.

Preceramic polymers can be used as coatings by depositing them on various substrates using various techniques. They can also be used to modify some of the properties by adding some layers of thickness to the substrate. They can be used to fabricate components having size of 1μm i.e. micro components. *[8]*

POLYMETHYL SILOXANE:

Polysiloxanes are surely the most important class of preceramic polymers and find their use in sealing applications .Generally denoted as Silicones the commercially available siloxanes are relatively cheap and variety of the derivatives are widespread in the commercial market which have extraordinary chemical, physical and electrical properties *[9-11]*. Besides their use as preceramic precursors, they are widely used in other more common applications like sealants, lubricants, adhesives and gaskets. They are generally odor- less, colorless, water resistant, chemical resistant, electrically insulating and stable at high temperatures *[10]*. Their higher thermal stability, together with relatively high melting and boiling points, make this class of polymers the preferred choice when organic polymers are not applicable. Typical applications are as sealants, coolants in transformers, long lasting motorinsulation, lubricants for bearings, foam-control agent in laundry detergents or as coatings to protect facades and historical monuments. Polysiloxanes are widely used even in other high-tech fields like aerospace industry, or as

protecting materials in the semiconductor industry, or during the processing of products like optical glass fibers, silicon wafers and chips. They are widely used as adhesion promoters in glues, sealants, pigments and paints, but also in the textiles and rubber industry. Moreover, their extremely low reactivity generally makes them non-toxic, and for this reason they can be used also in the personal care products industry, in biomedical applications like breast implants, or even as oral anti-foaming agent (e.g. simethicone) or as food additives. Their extremely interesting properties and the continuous development of this class of polymers, polysiloxanes market is expected to further grow and to find new applications, like for example as high oxygen permeable contact lenses, adhesive foams, synthetic fabric, waterproof membranes, process aids, or in lithographic applications.

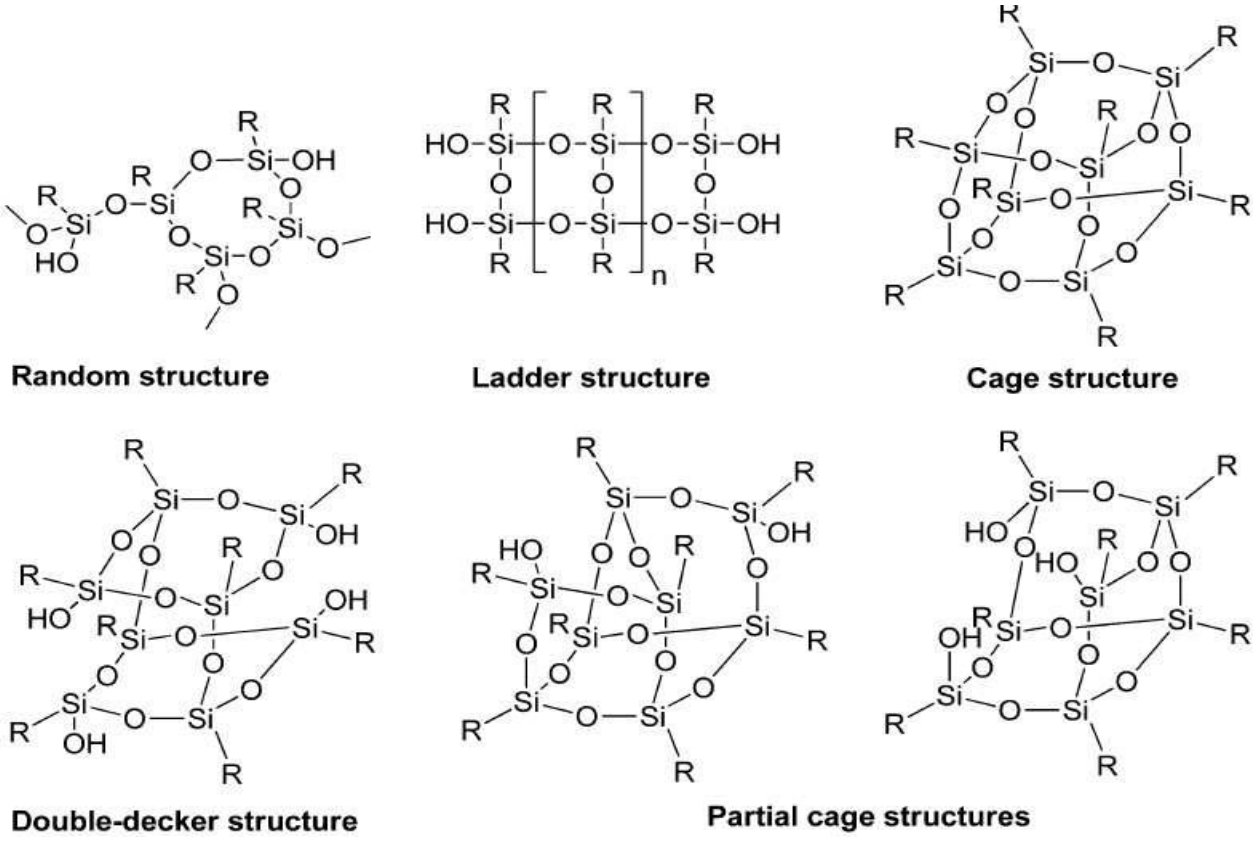


Figure 1.1 General types of poly (organosilsesquioxanes) [4]

1.2 Doped Polymer Derived Ceramics

Improvement in mechanical as well as thermal properties in silica glass by partial substitution of oxygen with Nitrogen and Carbon was initially approached through the conventional glass melting techniques , but the problems in there was the achievable carbon content which was at best 1 weight %. *[12]*

The sol-gel process derived precursors were also used to fabricate the oxycarbide glasses. In this method two organosilanes (triethoxysilane and methyl-diethoxysilane) were used to form the sol-gel precursor *[13-15]* through subsequent hydrolysis and condensation reaction. After pyrolysis in Argon atmosphere silicon oxycarbide glass is produced. Basically the Silicon Oxycarbide glasses consist of Si-O, Si-C bonds. Lower processing temperature and the presence of Si-C bond in the pyrolyzed form are the main advantages but lack of formation of crack free bulk bodies is the downside in this process.

During recent years a lot of studies are done on the modification of the Silicon Oxy-Carbide glasses by transition metal elements (Titanium *[16]*, Aluminum *[6]* etc.). The modification can be obtained by the reaction of preceramic polymers such as methylsilsesquioxane, methylphenylsilsesquioxane and modifier containing alkoxides forming a sol-gel process with some viable solvents so that molecular level of incorporation can be possible. After pyrolysis the ceramic system obtained in the polymeric route.

In the current dissertation attempt has been made to modify the siloxane structure by inculcating Aluminum and Titanium in molecular level at increasing level of metal to silicon ratio. The samples are pyrolyzed in flowing argon atmosphere at different temperatures in a tube furnace and the phase evolution in the glass structure is studied by X-Ray Diffraction technique. One

representative sample from the doped chemistry was evaluated for its oxidation resistance properties. The test at high temperature (up to 1450 ^{o}C) is done by DSC-TG analysis in the flowing Oxygen atmosphere.

For less amount doped into the Si- based PDCs in the chemical route the amorphous structure can be retained at pyrolysis temperature. There is a limit to this solubility in the amorphous nature of the siloxanes i.e. there is an optimal value of M: Si ratio (M= Al/Ti) after which amorphous nature is lost and more of the crystalline nature is obtained at the pyrolysis temperature.

In another note, there is always a question in the corner that where does the M reside in the structure of the glass. The hypothesis which is taken into account that the M- replaces the Si in the PDC structure, forming bonds with Carbon and Oxygen in basically the same way as the Si atom do. Simple bond counting method and bond energy measurement forms a favorable conclusion for the hypothesis made in the experimental analysis.

Chapter 2

LITERATURE REVIEW

LITERATURE REVIEW

What are PDCs?

Silicon based precursors, often termed as preceramic polymers on heat treatment produce Polymer Derived Ceramics (PDCs). The preceramic polymers are either carbosilanes, siloxanes or silazanes. Mostly carbosilanes produce binary compounds but for that matter siloxanes (containing Silicon-Oxygen ring structure *[1])* and silazanes produce ternary molecular networks of Si-C-O or Si-C-N. The main advantage being the high temperature stability these are highly desirable in the structural ceramics application *[2]*.

Ideally a precursor which is a cross-linkable liquid or a solid having melting and curing capability or soluble unmeltable is used. Broadly, there are five types of Silicon based polymeric precursors:

1. polysiloxanes: $[\text{-Si-O-Si-}]_n$
2. polysilsesquioxanes: $[RSiO_{1.5}]_n$
3. polysilanes: $[\text{-Si-Si-}]_n$
4. polycarbosilanes: $[\text{-Si-C-Si-}]_n$
5. polysilazanes: $[\text{-Si-N-Si-}]_n$

Among all sorts of polymers recorded above, polycarbosilanes and polysilazanes are most developed in research, as polycarbosilanes is the precursor of Si-C fibers that is first investigated by **Yajima** *et al* [21], and later turned to commercial manufacturing, and the latter is important for the formation of Si_3N_4 and Si-C-N ternary system.

Advantages over traditional method

Traditionally preparation of ceramics involved the use of powder technology route which usually needs sintering additives increasing the difficulties in technical uses. But in case of PDC route

very complex structures such as ceramic fibers can be realized which is not easily produced in powder technology. Above that high volume shrinkage in the drying process makes the powder technology process unsuitable.

A brief review of the research done in the last four decades was presented by Paolo Colombo et al *[4]* which exposes the readers about the application, process and various aspects of the polymer derived ceramics.

Processing of the polymeric precursors involves the steps of shaping and crosslinking, addition of inert fillers such as SiC or Si_3N_4 which eases the pressure occurrence in the system when the gases during the decomposition process are released followed by polymer to ceramic conversion.

Fabrication Parameters

The parameters which usually influence the fabrication of PDCs can be listed as follows

- The properties of the precursor which decides the shaping method.
- The degree of cross-linking of the polymer which directly influences the capability of plastic formation.
- The shape and dimension of the filler which may react with the matrix around.
- The fraction of oxygen present in the inert gas may hamper the process by eliminating the carbon containing phase and by producing oxides.
- Also the gas pressure which may resist the carbothermal reactions which occur at elevated temperature which leads to inhibition of crystallization.

Processes during cross-linking and pyrolysis

PDCs remain amorphous in the range of 1000 °C and 1800 °C. It depends on the structure and composition of the starting material. At high temperature, due to the devitrification of the amorphous network crystallization of various phases are obtained. Most of the cases the after decomposition crystallization along with phase separation occurs with the release of gaseous products such as CO, SiO, N_2 etc. [4]

Application of PDCs

PDCs have found their application in many key areas which include fiber technology, ceramic matrix composites, porous components production, environmental barrier coating, microcomponents, pressure sensors and various machinable components in the space research fields. Introduction of B and N enhances the amorphous nature of the SiC fibers which remains the same until 1700 °C and having great oxidation and creep resistance *[25]*.

Doping in the SiCO/SiCNO structure

K. Terauds *et al [5],* were successful in producing Hf-Si-C-NO in polymeric route by using relatively easy process of molecular level mixing of a silazane (Ceraset) and a hafnium alkoxide(hafnium tert- butoxide) and subsequent during and pyrolysis of the mixture. The main aim was to find out up to which solubility of hafnia in the structure, which was determined by gradually increasing the Hf- content in the structure. They found out the optimal value of the Hf/Si to be 22% up to which Hafnia remains soluble and after that starts to crystalize at pyrolysis temperature. The hypothesis proposed was that the Hf substitutes Si in the ceramic structure which was backed by simple bond counting method and bond energies evaluation which was found to be quite feasible.

Ralf Riedel *et al [6]*, has reported a bulk preparation of Si-Al-O-C ceramics from pyrolysis of a commercially available siloxane precursor i.e. MK. The cross linking agent used in the process was Zr- acetylacetonate and the alumina modifier used in the process was an alkoxide of Alumina commercially known as Alumatrane ($C_6H_{12}NO_3Al$). The team produced three samples in increasing weight percent of aluminum (i.e. 9% Al, 16% Al. 23% Al) in the structure. After warm pressing of the samples obtained by warm pressing pellets were formed. The characterization of the samples after pyrolysis at different temperatures were done. The green bodies formed in the process were mechanically stable and transparent. Thermo gravimetric Analysis of the un doped and doped samples suggest that the weight loss varies between 21 to 30%. The gases that evolve in the process were mainly methane and hydrogen which involves the splitting of bonds between Si-C and C-H. They were successful in producing dense crack free Si(Al)OC in the process. The viscoelasticity behavior of the polymers plays a pivotal part in the formation of crack free surface in the warm pressing method. The high temperature resistance of the Si(Al)OC ceramics was determined when compared with Al- free counterpart. At elevated temperatures the ceramics undergo phase separation and densification. The important conclusion they got was the crack free bulk at higher temperature up to 1700^{o}C, which is quite impressive.

Rishi Raj *et al [7]*, have researched about the oxidation behavior of the hafnium modified PDC, HfSiCNO up to 1600^{o}C. Crystallization of the previously amorphous phase was observed in the XRD analysis. The oxide overgrowth is observed as precipitates of hafnia/hafnon and the interioris mainly composed of nanoscale domains of hafnia. The overgrowth thickness of the uncoated SiC-SiC mini composites and the SiCNO and HfSICNO coated were compared. They concluded that at high temperature Hafnia/hafnon precipitate is obtained which is arranged in a necklace like

structure in the structure. Geometrical models have been proposed which changes weight changes data into oxide overgrowth thickness.

Kleebe *et al [8]*, studied the phase separation of SiCO glass which depicts the phase separation of that SiCO glass at temperature excess of 1200 °C. Formation of SiO_2 and silicon carbide based environments was observed. At temperature above 1300 °C nano sized silicon carbide particles were also found in the Transmission Electron Microscopy (TEM) study. Due to the high temperature phase separation densification along with pore elimination was observed. The limiting working temperature of stoichiometric SiCO glass was found to be between 1100 °C and 1150 °C. Cristobalite was not found at the temperature > 1200 °C. High amount of free carbon in the amorphous silica structure prevents the formation of cristobalite because the short range inhibition caused due to the introduction of carbon in the silica structure.

Linan an *et al [23]*, proposed a model based on the experimental by diffusion of oxygen through pure silica and aluminum doped amorphous silica. Oxide formation was carried out by the oxidation of polymer-derived SiCN and SiAlCN ceramics. The precursor used was a silazane (ceraset) and the aluminum modifier used was an alkoxide (Aluminum isopropoxide). Small amount of aluminum incorporation in the structure lead to the inhibition of oxygen diffusion in the structure. The energy required to initiate the network diffusion for aluminum doped silica is obtained to be nearly two times higher than that of pure silica. Hence new structural model in which Al is placed at the center of the rings which is formed by six SiO_4 tetrahedras was proposed.

R. Kempe *et al [24]*, reported the modification of ceramics with the late transition metals along with the elements from group 8-11(Fe, Co, Ni, Pd etc.). The synthesis of metal modified PDCs can be obtained mainly through the mixing of the precursors with the required metal oxide powders, by modifying precursor polymers using the coordination compound. The first process

mainly is simply mixing of powders along with the polymer followed by cross-linking and pyrolysis. The second method involves pyrolysis of metallopolymers which have metallic atom and monomer and after subsequent pyrolysis process metal modified ceramics were obtained. In the last process coordination compound after reaction with the polymeric precursor due to transformation of metal to the polymer chain produces metal modified which after cross-linking and pyrolysis forms metal modified PDCs. Application of Iron modified PDCs are detailed which is due to their good magnetic properties.

Chapter 3

EXPERIMENTAL

3. EXPERIMENTAL WORK

3.1 ***Batch Preparation***

3.1.1 Modification of siloxane system by Aluminum

Modification of poly methylsilsesquioxane polymer was done by introducing measured amount of Al. Al was introduced in the molecular level. The Al was varied 5, 10, 15 and 25 mole % and the batch calculations are as follows:

Batch 1: Al/Si = 0.05, Nomenclature: 5AS

The Al and Si ratio in this batch is chosen as 5%. In a beaker 20ml of isopropanol is taken in which 0.70 gm of aluminum iso-propoxide is added and is then magnetically stirred until it completely dissolves. After the dissolution of the aluminum modifier 5gm of polymer (MK) is added and the solution is further magnetically stirred. 1 weight percent of cross linking agent is added for the crosslinking for the further steps.

Batch 2: Al/Si = 0.10, Nomenclature: 10AS

The Al and Si ratio in this batch is chosen as 10%. In a beaker 20ml of isopropanol is taken in which 1.40 gm of aluminum iso-propoxide is added and is then magnetically stirred until it completely dissolves. After the dissolution of the aluminum modifier 5gm of polymer (MK) is added and the solution is further magnetically stirred. 1 weight percent of cross linking agent is added for the crosslinking for the further steps.

Batch 3: Al/Si = 0.15, Nomenclature: 15AS

The Al and Si ratio in this batch is chosen as 15%. In a beaker 20ml of isopropanol is taken in which 2.10 gm of aluminum iso-propoxide is added and is then magnetically stirred until it

completely dissolves. After the dissolution of the aluminum modifier 5gm of polymer (MK) is added and the solution is further magnetically stirred. 1 weight percent of cross linking agent is added for the crosslinking for the further steps.

Batch 4: Al/Si = 0.25, Nomenclature: 25AS

The Al and Si ratio in this batch is chosen as 25%. In a beaker 20ml of isopropanol is taken in which 3.50 gm of aluminum iso-propoxide is added and is then magnetically stirred until it completely dissolves. After the dissolution of the aluminum modifier 5gm of polymer (MK) is added and the solution is further magnetically stirred. 1 weight percent of cross linking agent is added for the crosslinking for the further steps.

A polymer: isopropy alchohol ratio of 5gm: 20ml of is kept constant for all the mixture.

Nomenclature	MK(gm)	AIP(gm)	IPA(ml)	Al/Si
MK	5	0	20	0
5AS	5	0.70	20	0.05
10AS	5	1.40	20	0.10
15AS	5	2.10	20	0.15
25AS	5	3.50	20	0.25

Table 2.1 Batch calculation of Al- modified polymer samples

Drying

The batches are dried at 60^{o}C for overnight, so that a solid form of silica alumina nano composite structure is obtained after the solvent removal. In which nano sized filler are homogenously distributed throughout.

Cross Linking

Crosslinking agent Triethylamine (TEA) is added in the former steps during the mixing process of the batch preparation. The crosslinking is done at 350^{o}C for 2hours in order to obtain a rigid polymer which is not fusible during pyrolysis at high temperatures when the polymer converts to final ceramic material.

Milling

The cross linked resins are ground using a mortar and pestle and is further milled to obtain a powder of some extent. Then the moderately milled samples are milled thoroughly in the SPEX Mill (1080 RPM) for 20 minutes per sample. The powder obtained was collected in different zip covers.

Pyrolysis

The samples are placed in the crucible and carefully put in to the tube furnace. Samples were sintered at different temperatures such as 1000 ^{o}C, 1200 ^{o}C and 1400 ^{o}C under flowing Argon. The phase evolution at each temperature is studied thoroughly. The oxidation resistance test of a particular aluminum modified batch (10AS) is done for the pyrolyzed samples which are further pyrolyzed under flowing air at 1000 ^{o}C.

FLOW CHART OF THE EXPERIMENTAL WORK

Calculated amount of Aluminum IsoPropoxide is mixed in Iso Propyl Alchohol

↓

The mixture is magnetically stirred until a clear solution is obtained

↓

A fixed amount of Polymer(MK) is added in the solution and is further stirred

↓

1 weight % of Crosslinking agent (TEA) is added

↓

The obtained solution is dried in the Oven at 60^{o}C for overnight.

↓

The samples are crosslinked at 350^{o}C for 2 hours.

↓

Obtained solid crosslinked resin is crushed into powder using Mortar & pestle.

↓

The samples are further milled in a high energy SPEX Mill for further 20 mins.

↓

Samples are sintered at different temperatures and was characterized.

Flow Chart 1: Process of fabrication of Al- modified SiOC

3.1.2 Modification of siloxane system by Titanium

Modification of poly methylsilsesquioxane polymer was done by introducing measured amount of Ti. Ti was introduced in the molecular level. The Ti was varied 5, 10, 15 and 20 mole % and the batch calculations are as follows:

Batch 1: Ti/Si = 0.05, Nomenclature: 5TS

The Ti and Si ratio in this batch is chosen as 5%. In a beaker 20ml of isopropanol is taken in which 1.90 ml of titanium iso-propoxide is added and is then magnetically stirred until it completely dissolves. After the dissolution of the Titanium modifier 10gm of polymer (MK) is added and the solution is further magnetically stirred. 1 weight percent of cross linking agent is added for the crosslinking for the further steps.

Batch 2: Ti/Si = 0.10, Nomenclature: 10TS

The Ti and Si ratio in this batch is chosen as 10%. In a beaker 20ml of isopropanol is taken in which 3.80 ml of titanium iso-propoxide is added and is then magnetically stirred until it completely dissolves. After the dissolution of the Titanium modifier 10gm of polymer (MK) is added and the solution is further magnetically stirred. 1 weight percent of cross linking agent is added for the crosslinking for the further steps.

Batch 3: Ti/Si = 0.15, Nomenclature: 15TS

The Ti and Si ratio in this batch is chosen as 15%. In a beaker 20ml of isopropanol is taken in which 5.70 ml of titanium iso-propoxide is added and is then magnetically stirred until it completely dissolves. After the dissolution of the Titanium modifier 10gm of polymer (MK) is

added and the solution is further magnetically stirred. 1 weight percent of cross linking agent is added for the crosslinking for the further steps.

Batch 4: Ti/Si = 0.20, Nomenclature: 20TS

The Ti and Si ratio in this batch is chosen as 20%. In a beaker 20ml of isopropanol is taken in which 7.60 ml of titanium iso-propoxide is added and is then magnetically stirred until it completely dissolves. After the dissolution of the Titanium modifier 10gm of polymer (MK) is added and the solution is further magnetically stirred. 1 weight percent of cross linking agent is added for the crosslinking for the further steps.

A polymer: isopropanol ratio of 10gm: 20ml of is kept constant for all the mixture.

Nomenclature	MK(gm)	TIP(ml)	IPA(ml)	Ti/Si
5TS	10	1.90	20	0.05
10TS	10	3.80	20	0.10
15TS	10	5.70	20	0.15
20TS	10	7.60	20	0.20

Table 2.2: Batch calculation of Ti- modified polymer samples

Drying

The batches are dried at 60 ^{o}C for overnight, so that a solid form of silica alumina nano composite structure is obtained due to the solvent removal. In which nano sized filler are homogenously distributed throughout.

Cross Linking

Crosslinking agent Triethylamine (TEA) is added in the former steps during the mixing process of the batch preparation. The crosslinking is done at 350 ^{o}C for 2hours in order to obtain a rigid polymer which is not fusible during pyrolysis at high temperatures when the polymer converts to final ceramic material.

Milling

The cross linked resins are ground using a mortar and pestle and is further milled obtain a powder of some extent. Then the moderately milled samples are milled thoroughly in the SPEX Mill (1080 RPM) for 20 minutes per sample. The powder obtained was collected in different zip covers.

Pyrolysis

The samples are placed in the crucible and carefully put in to the tube furnace. Samples were sintered at different temperatures such as 1000 ^{o}C, 1200 ^{o}C, 1400 ^{o}C and 1500 ^{o}C under flowing Argon. The phase evolution at each temperature is studied thoroughly. The oxidation resistance test of a particular titanium modified batch (10TS) is done for the pyrolyzed samples which are further pyrolyzed under flowing air at 1000 ^{o}C.

FLOW CHART OF THE EXPERIMENTAL WORK

Calculated amount of Titanium iso-propoxide(l) is mixed in isopropanol

The mixture is magnetically stirred until a clear solution is obtained.

A fixed amount of Polymer(MK) is added in the solution and is further stirred

1 weight % of Crosslinking agent (TEA) is added

The obtained solution is dried in the Oven at 60^{o}C for overnight.

The samples are crosslinked at 350^{o}C for 2 hours.

Obtained solid crosslinked resin is crushed into powder using Mortar & pestle.

The samples are further milled in a high energy SPEX Mill for further 20 mins.

Samples are sintered at different temperatures and was characterized.

Flow Chart 2 Process of fabrication of Ti- modified SiOC

3.2 CHARACTERIZATION

3.2.1 Phase evolution Analysis

The presence of different kind of phases in the sample powder is known from the X-ray diffraction measurement of powder. When X-rays passes through matter, the radiation interacts with the electrons in the atoms, resulting in scattering of the radiation as shown in Figure 3.2. For crystalline materials the distances between the planes is same and if the atoms are of the same magnitude as the wavelength of the X-rays.

The institute XRD machine (Rigaku, Ultima IV, X-Ray diffractometer) was used to study the phase evolution characteristic. After milling the pyrolyzed samples, they were placed in a sample holder. The sample holder and the glass slides used were cleaned with acetone thoroughly. XRD plot was obtained from 15^0 to 70^0 at a scanning rate of 20^0/min.

Figure 3.1: XRD Machine

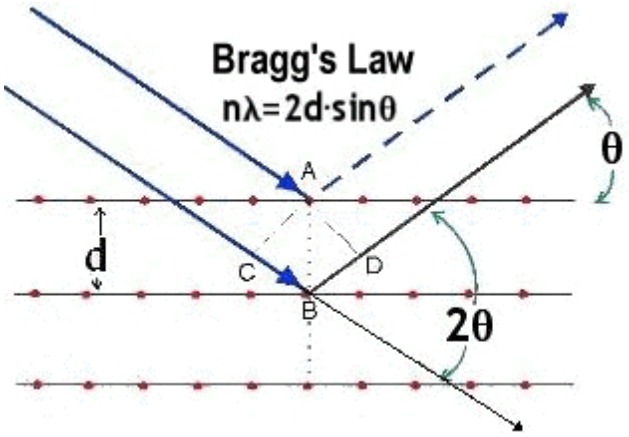


Figure 3.2 *Principle of X-Ray Diffraction [16]*

3.2.2 Differential Scanning Calorimetry (DSC)

The operating principle of DSC

There are separate containers for both sample and reference, and associated with each are individual heating elements as well as temperature measuring devices. Both cells are surrounded by a refrigerated medium (usually via flowing water) which permits rapid cooling.

The sample and reference chambers are heated equally into a temperature regime in which a transformation takes place within the sample. As the sample temperature infinitesimally deviates from the reference temperature, the device detects it and reduces the heat input to one cell while adding heat to the other, so as to maintain a zero temperature difference between the sample and reference, establishing a "null balance". The quantity of electrical energy per unit time which must be supplied to the heating elements (over and above the normal thermal schedule), in order to maintain this null balance, is assumed to be proportional to the heat released per unit time by the sample. The y- axis in the plot is expressed in terms of energy per unit time.

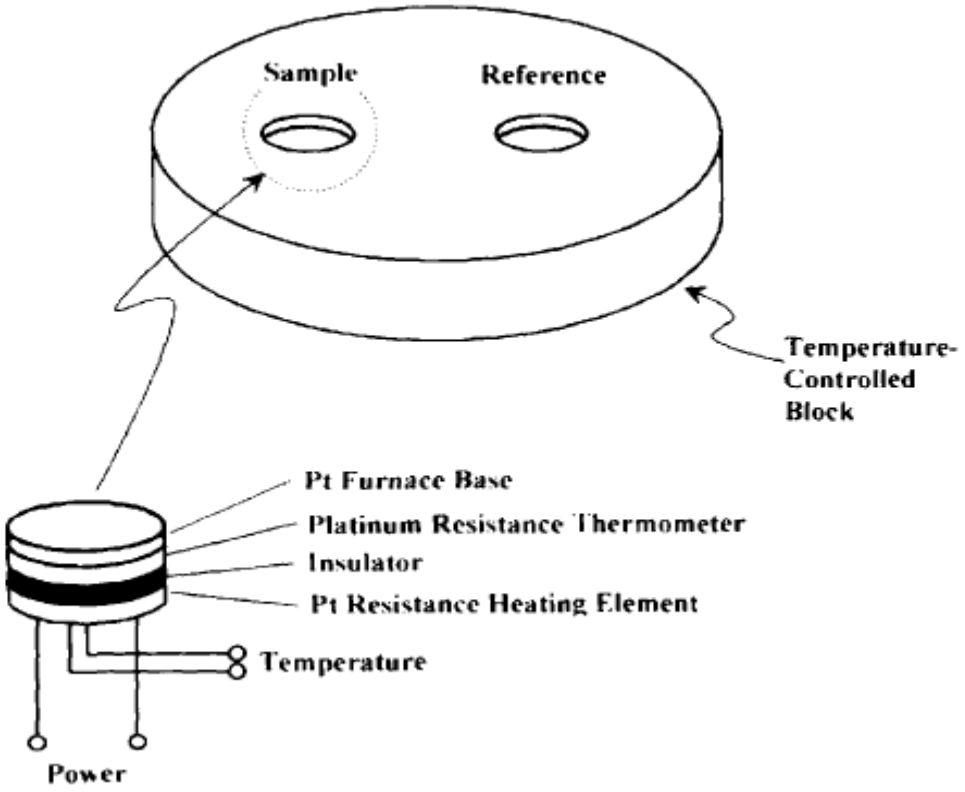


Figure 3.3 Schematic of principle of DSC *[17]*

The DSC has generally two control cycle portions. One portion strives to maintain the null balance between sample and reference, while the other strives to keep the average of the sample and reference temperature at the set point. These processes switch back and forth quickly so as to maintain both simultaneously.

3.2.3 Thermo gravimetric Analysis (TGA)

Thermo gravimetric analysis (TGA) is the study of weight changes of a specimen as a function of temperature. The technique is useful strictly for transformations involving the absorption or evolution of gases from a specimen consisting of a condensed phase. Most TG devices are configured for vacuum and variable atmosphere. The balances associated with TG's are highly

sensitive, with very small resolution in the micrometer range. These instruments can be used for a wide variety of investigations, from the decomposition of clays to high temperature oxygen uptake in the processing of superconducting materials. In our experiment we have used the analysis to calculate the loss in the material when processed at high temperature (up to 1450^{o}C) in inert (Ar) atmosphere.

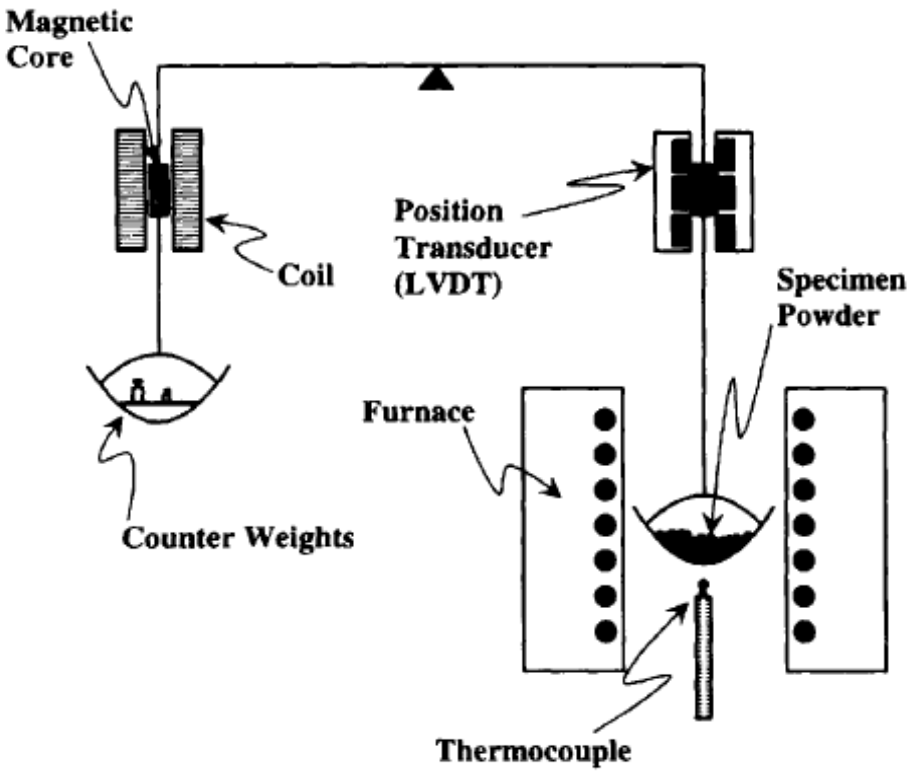


Figure 3.4 Schematic of principle of TGA *[18]*

The specimen powder is placed on a refractory platinum pan. The pan, in the hot zone of the furnace, is suspended from a high precision balance. A thermocouple is in close proximity to the specimen but not in contact, so as not to interfere with the free float of the balance. The balances are electronically compensated so that the specimen pan does not move when the specimen gains or loses weight.

If reacted gases are passed through the specimen chamber or gases are released by the specimen, the chamber containing the balance is often maintained at a slightly more positive pressure via compressed air or inert gas; this is to protect the balance chamber and its associated electronic components from exposure of corrosive gases.

Chapter 4

RESULTS & DISCUSSIONS

RESULTS AND DISCUSSIONS

4.1 Thermal behavior of poly methyl silsesquioxane

Poly methyl silsesquioxane on pyrolysis in inert atmosphere at high temperatures forms ceramics which are one form of polymer derived ceramics.

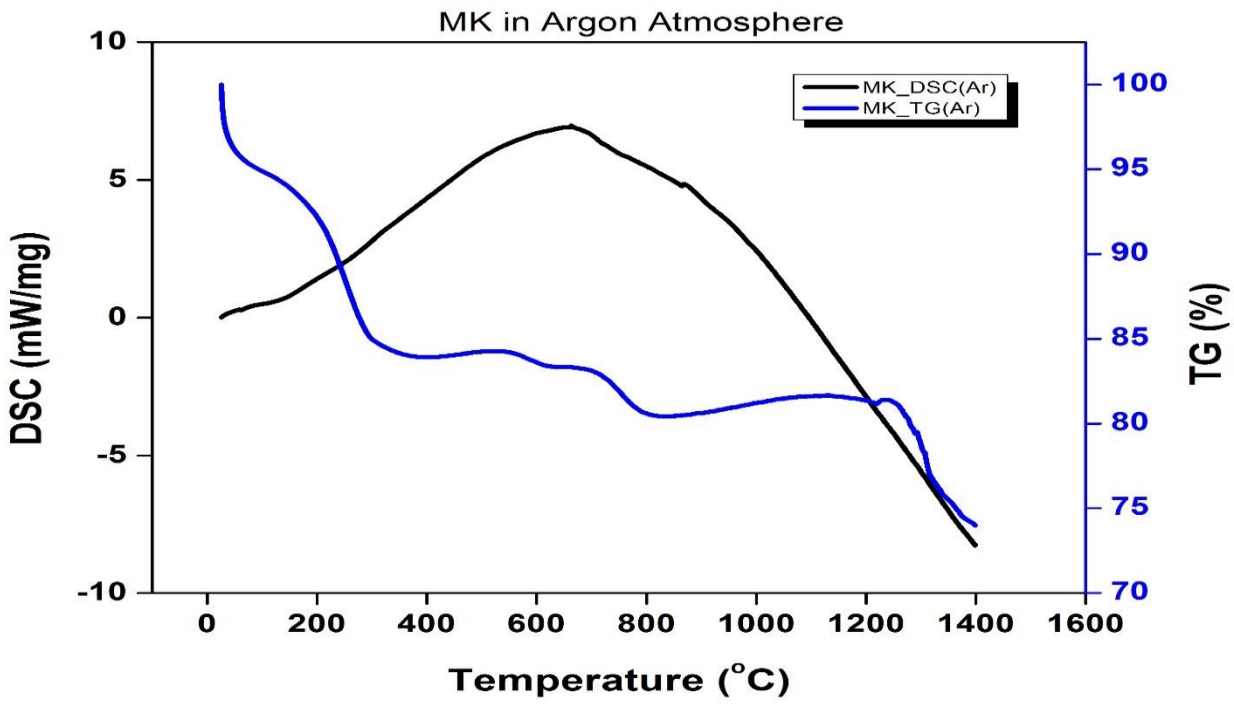


Figure 4.1 DSC-TG of cross-linked MK polymer up to 1450 °C in Argon atmosphere

The polymer to ceramic conversion was investigated by thermogravimetry. The catalyst added polymer on crosslinking shows the TG graph as shown in the Figure 4.1. There are mainly 3 regions of interest namely from RT to 400 °C (~14% wt. loss), 400 °C to 800 °C (6% wt. loss), 800 – 1250 °C (which is primarily loss free, but exhibits subtle weight gain) and above 1200 °C (6% wt. loss). The first weight loss is due to the release of water, ethanol and methanol, while the further weight losses are due to the release of hydrogen and methane from the system. *[20]*

4.2 Phase evolution in unmodified silicon oxycarbide

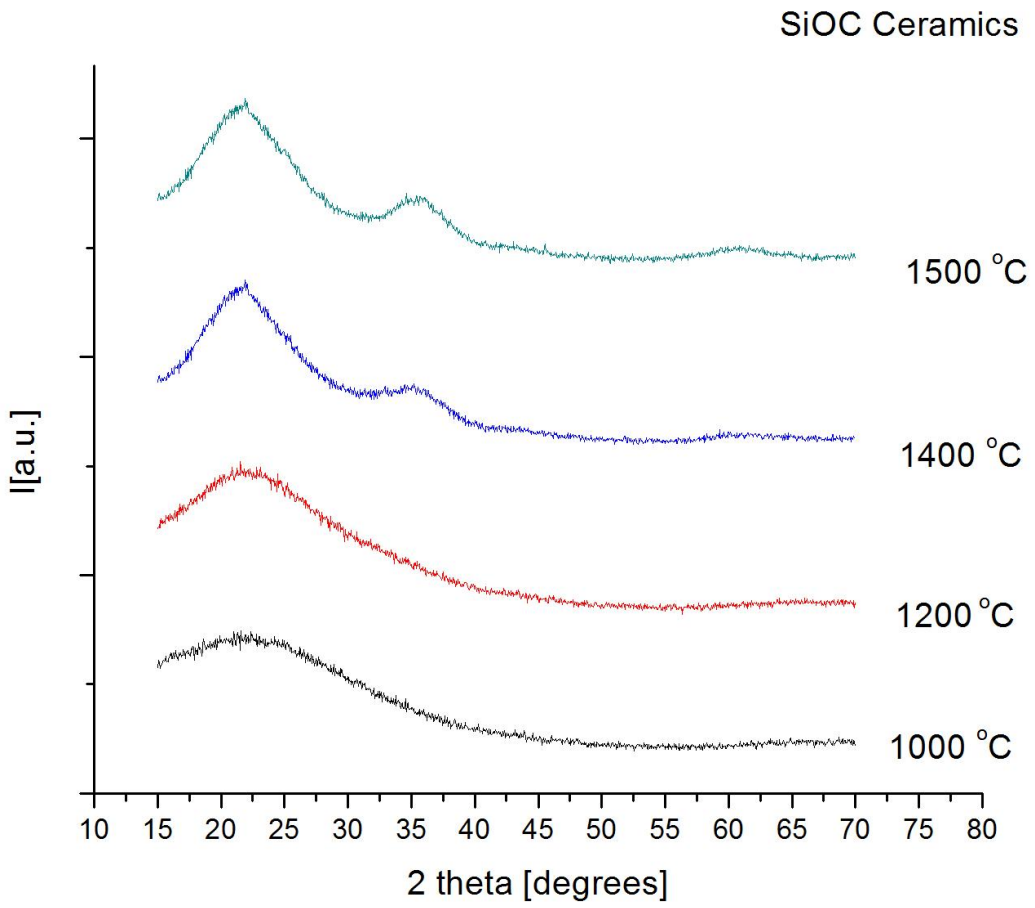


Figure 4.2 XRD Analysis of unmodified silicon oxycarbide at different temperatures

Pure silicon oxycarbide was fabricated by inert atmosphere pyrolysis of polymethyl silsesquioxane (PMS). The catalyst (TEA) was added during the mixing process for better crosslinking. As shown in the figure 4.2, at 1000 °C the amorphous nature of the SiCO is retained and there is no phase separation is observed. As the temperature is increased to 1200 °C the same pattern is observed and no change in amorphous nature is observed. At higher temperature i.e. 1400 °C also there is no major change in the amorphous nature However the broad peak at about 22° of 2Θ appears yo have a sharper profile. In addition there is the emergence of the broad peak at 2Θ of 36°. The first peak is assigned to cristobalite. Therefore for the 1400 °C pyrolyzed SiCO, it is logical to conclude

that the SiO_2 based nano domains in the amorphous SiCO structure are getting progressively bigger. However, the intensity indicates that the ceramics cannot be still considered to be a crystalline solid. The peak at 36° is indicative of the formation of β-SiC nanocrystal from the phase separation of the SiCO ceramics into SiO_2 and β-SiC. The XRD spectrum for the 1500 °C pyrolyzed powder was almost like that of the 1400 °C powder, with an additional appearance of a small and very broad signal at ~60° of 2Θ. This further corroborates the formation of β-SiC as the peak can be correlated with SiC.

4.3 XRD Analysis of modified at different Temperatures

4.3.1 Aluminum modified SiOC

All the batches pyrolyzed @1000 °C

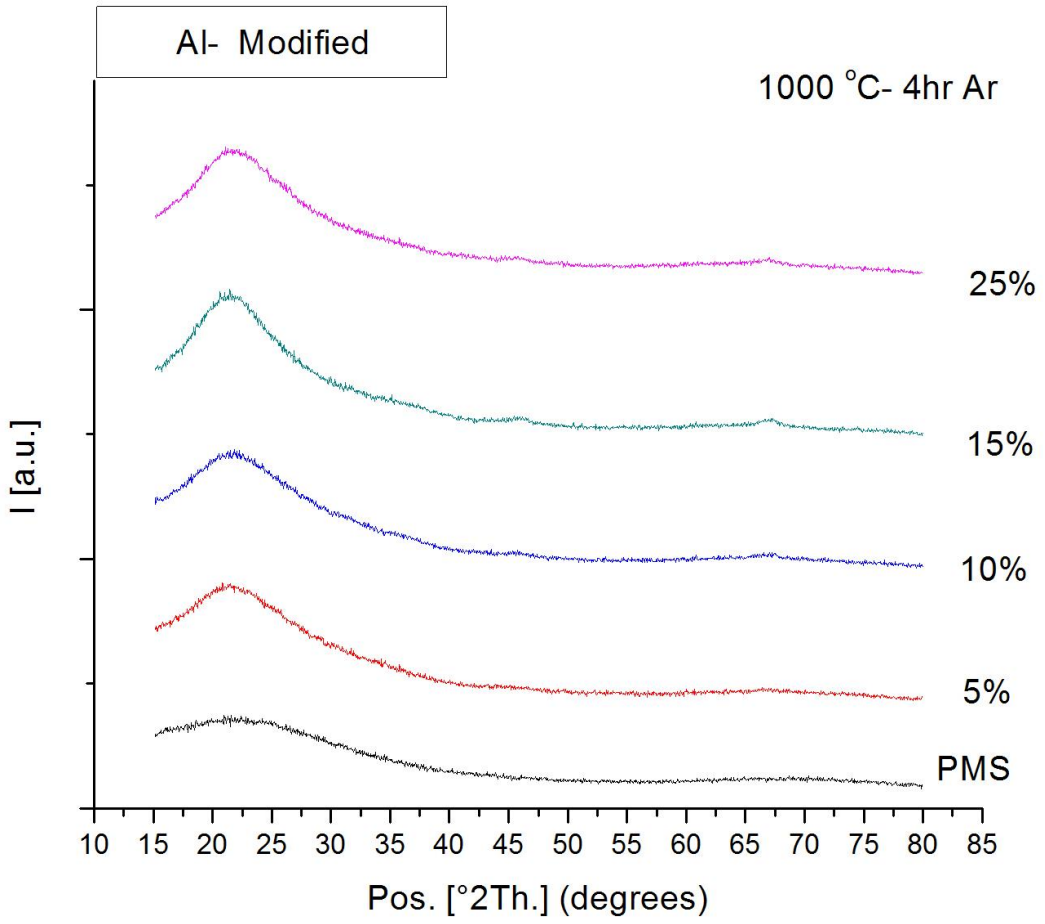


Figure 4.3: XRD analysis of different Al- modified compositions pyrolyzed at 1000 °C

Figure 4.3 shows the patterns obtained after the different composition samples (5AS, 10AS, 15AS, 25AS) pyrolyzed at 1000 °C. The pattern indicates that the amorphous nature of the samples is not changed even after pyrolysis temperature. One big hump of cristobalite is observed in the XRD patterns and no crystallization of Al containing materials thus Aluminum cations are in the amorphous state. Increasing the Al content doesn't affect the amorphous nature at this temperature.

No phase separation whatsoever was observed by changing the amount of Al content in this temperature and the samples remain amorphous.

All the batches pyrolyzed @1200 °C

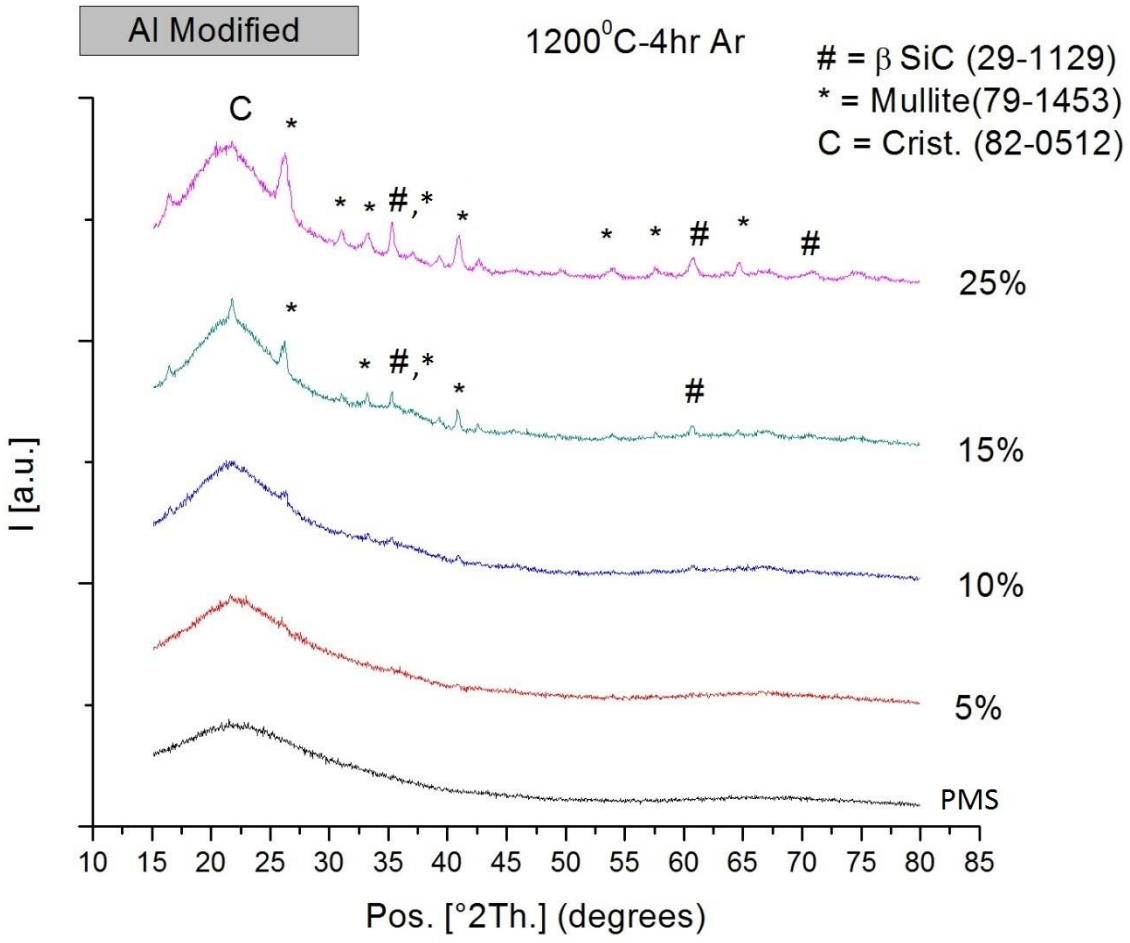
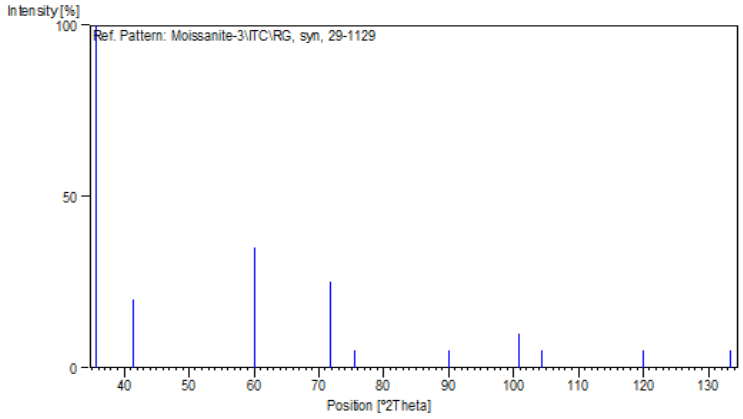
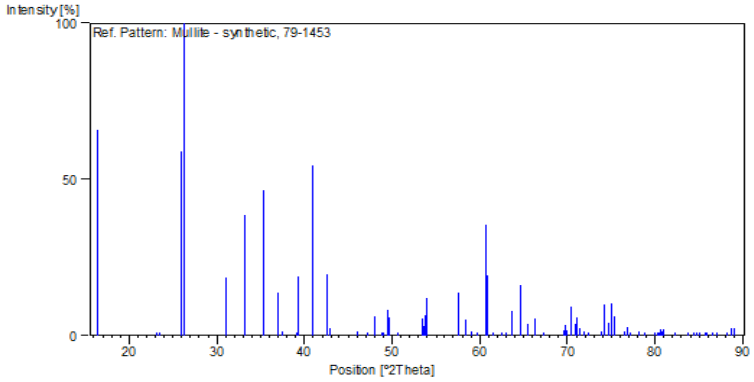


Figure 4.4: XRD analysis of different Al- modified compositions pyrolyzed at 1200 ^oC

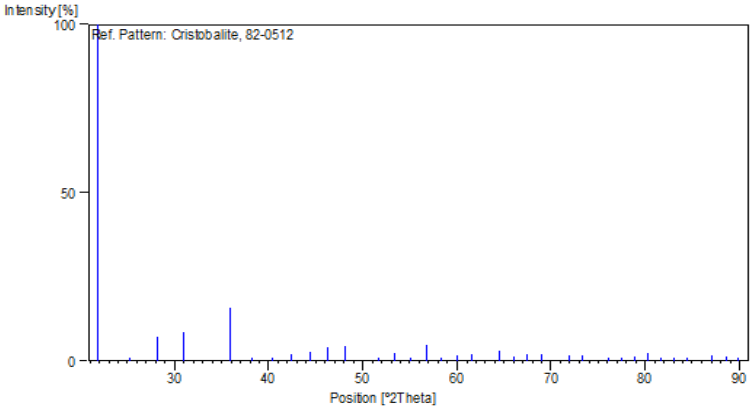
Standard Files



(a)



(b)



(c)

Figure 4.5 Standard files of (a) Moissanite (29-1129), (b) Mullite (79-1453), (c) Cristobalte (820512)

Figure 4.4 which is the XRD analysis of the batches which were pyrolyzed at 1200 ^{o}C. The amorphous nature of the sample pyrolyzed at 1200 ^{o}C is retained until a certain amount of doping of the cation in to the matrix. Up to 10% of Aluminum can be introduced in the matrix without causing any change in the amorphous nature of SiCO. On increasing the Al- content up to 15%, however first signs of the formation of mullite is observed along with formation of β silicon carbide at this temperature. By comparing the standard files shown in the figure 4.5 with the obtained XRD analysis in the Figure 4.4, the 100% relative intensity peak of β SiC is observed at ~35° 2 theta value and the next intense peaks are found at 60°, ~72° in the X axis which can be found in the XRD analysis graph. Similarly mullite has the 100% relative intensity peak at 26° 2 theta and thus in figure 4.4 the aluminum rich SiCO has mullite in the phase. Formation of mullite is clearer as the doping amount is increased from 5% to 25 % in the SiCO structure.

On further increasing in the Aluminum content up to 25% the β SiC peaks are clearly visible and mullitization is clearly observed. Comparing with the undoped SiCO (PMS) pyrolyzed at 1200 ^{o}C and the corresponding 25AS, no trace of Alumina peak was observed but mullitization along with formation of β SiC is observed. No phase separation was observed until the aluminum content reaches 15% where the nanocrystalline Mulite and, β SiC phase was observed.

All the batches pyrolyzed @1400°C

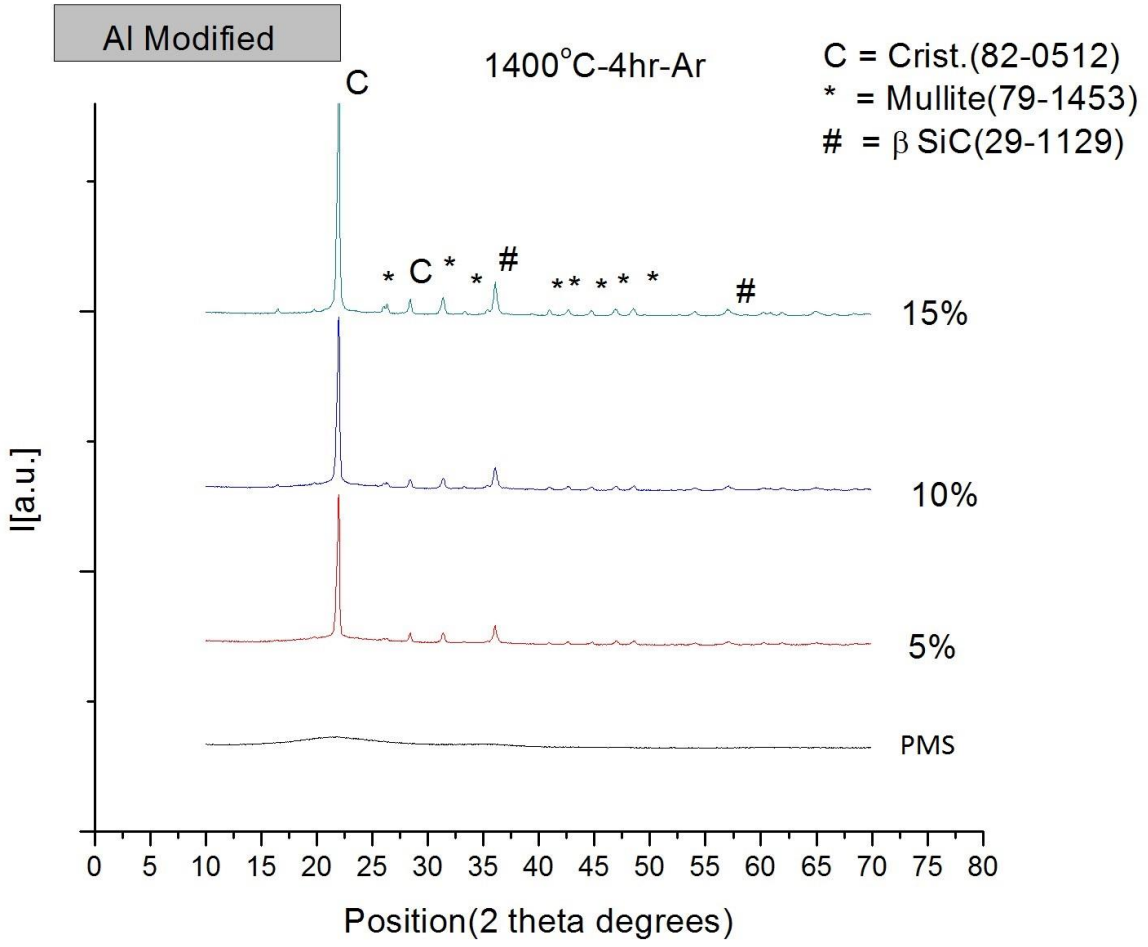


Figure 4.6: XRD analysis of different Al- modified compositions pyrolyzed at 1400 °C

Figure 4.6 depicts the XRD analysis of the various compositions listed on Table 3.1 pyrolyzed at 1400 °C. Clear peaks of cristobalite are obtained and mullitization occurs even in the lowest amount of doping of Al (i.e. in 5AS). Silicon carbide is also formed at this pyrolysis temperature. Comparing to the MK XRD analysis at this temperature we can conclude that though the pure silicon oxycarbide is amorphous in nature but as the doping amount of Al- is increased gradually

the mullitization occurs along with the retention of C in the structure by the formation of silicon carbide.

4.3.2 Titanium modified SiOC

All the batches pyrolyzed @1000°C

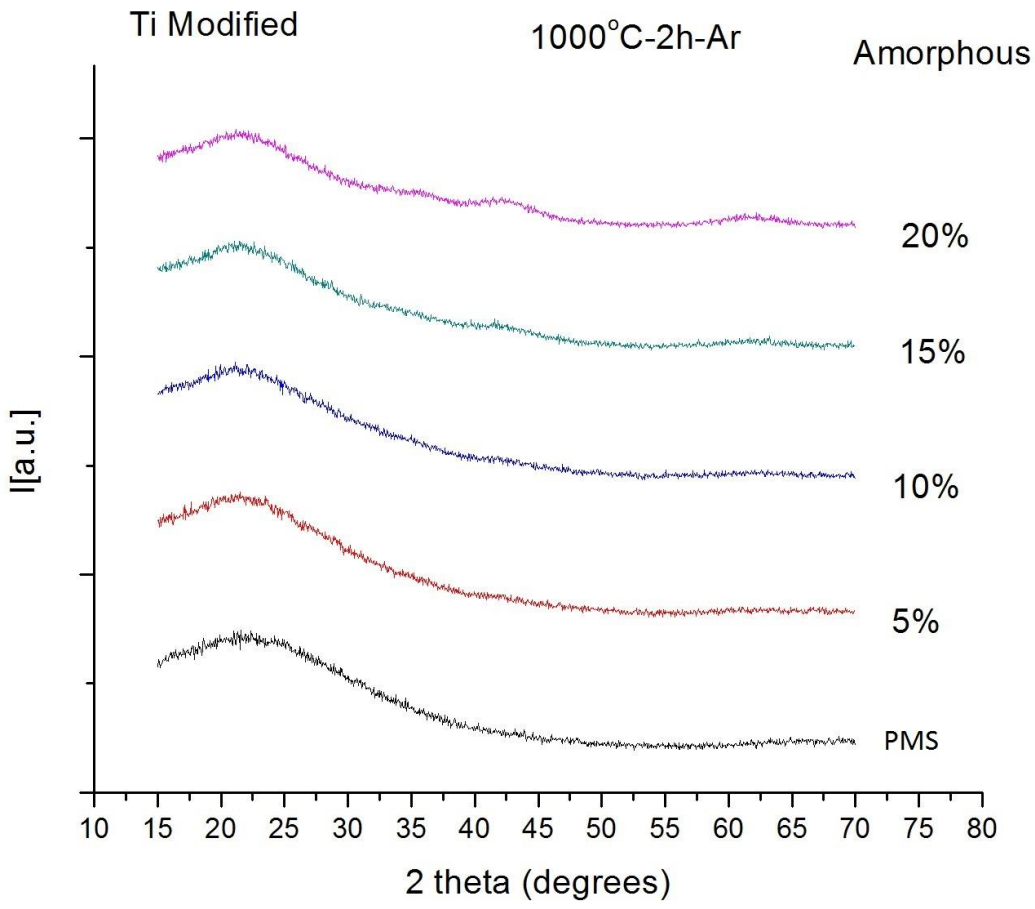


Figure 4.7: XRD analysis of different Ti- modified compositions pyrolyzed at 1000 °C

Figure 4.7 shows the patterns obtained after the different composition samples (5AS, 10AS, 15AS, and 25AS) pyrolyzed at 1000°C. The pattern indicates that the amorphous nature of the samples is not changed even after pyrolysis temperature. One broad hump of cristobalite is observed in the

XRD patterns and no Ti containing materials thus Ti cations are in the amorphous state. Increasing the Ti content doesn't affect the amorphous nature at this temperature. No phase separation whatsoever was observed by changing the amount of Ti content in this temperature and the samples remain amorphous.

All the batches pyrolyzed @1200°C

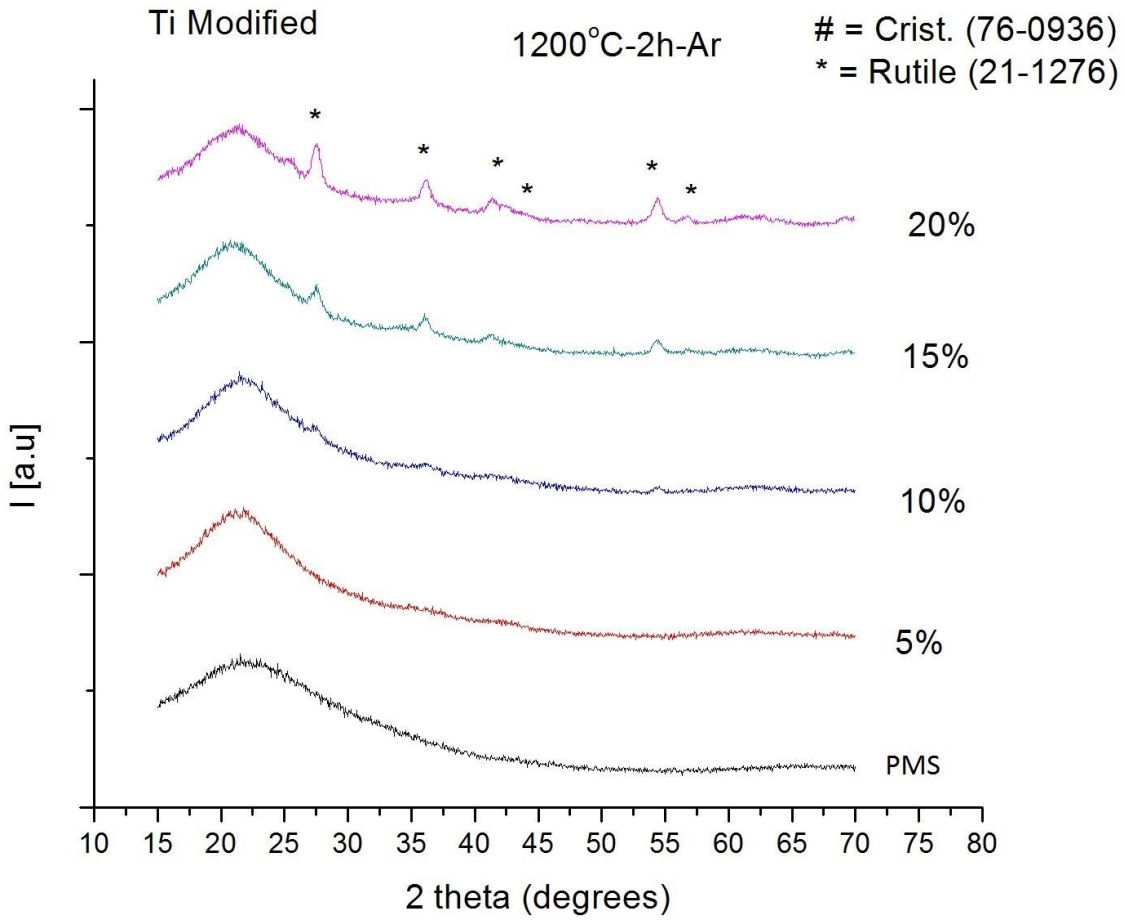
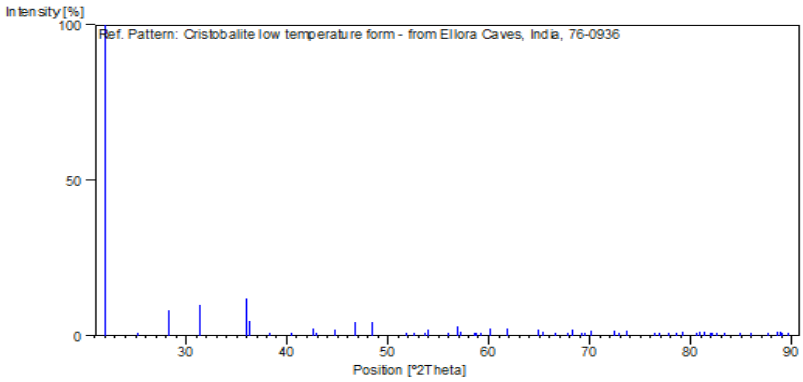
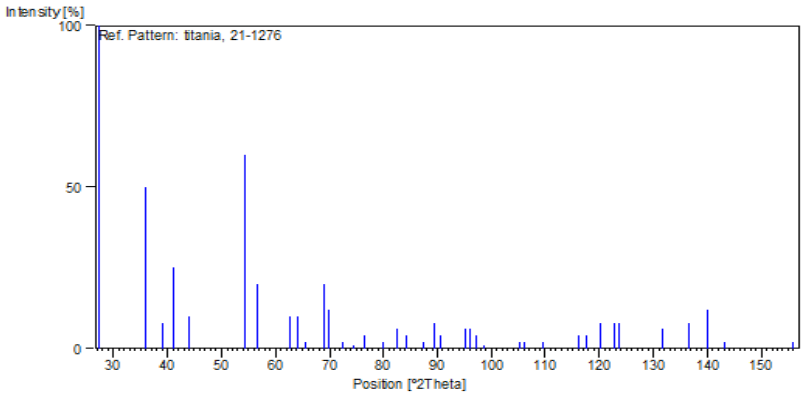


Figure 4.8: XRD analysis of different Ti- modified compositions pyrolyzed at 1200°C

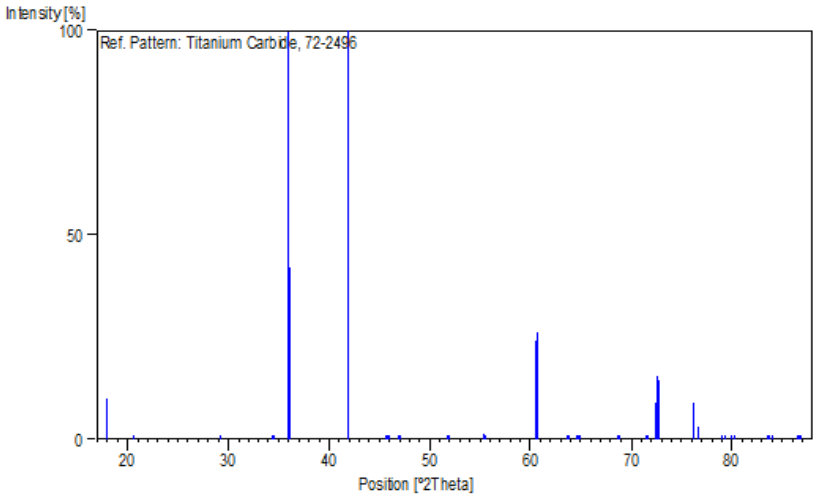
Standard Files



(a)



(b)



(c)

Figure 4.9 Standard files of (a) Cristobalite (76-0936), (b) Titania (21-1276), (c) Titanium Carbide(72-2496)

The XRD analysis of the Ti- modified silicon oxy-carbide pyrolyzed at 1200 °C is shown in the Figure 4.8. The undoped SiCO ceramics is amorphous in nature denoted as PMS in the figure. As the titanium concentration is increased in the system the 1200 °C pyrolyzed batch show amorphous nature up to there is a doping of 10 % Ti in the system. But when the doping amount was increased up to 15%, faint peaks referring to TiO_2 begin to emerge. The 100% relative intensity peak of rutile (21-1276) as shown in the standard file 4.9(b) is seen at 27.5° 2 theta value which can be seen in the 15% Ti doped SiCO. Other relative intensity peaks are 37.5°, 42.5° and 57.5° in the figure which can be matched with the XRD analysis graph. So, increasing the Ti concentration up to 15 % initiate the phase separation, which is clearly seen in the 20% Ti- doped SiCO. The amorphous system phase separates into SiCO and TiO_2 .There is no sign of formation of either silicon carbide or titanium carbide in the system as can be seen by comparing the standard file attached in the figure 4.5 and 4.9. It appears that at this stage of pyrolysis, the SiCO glass accommodates certain molecular percentage of Ti atoms into the glass network (which is evidently about 10%). Additional Ti, if doped in excess of the bulk glass solubility limit, phase separates into the oxide (i.e. TiO_2).

All the batches pyrolyzed @1400°C

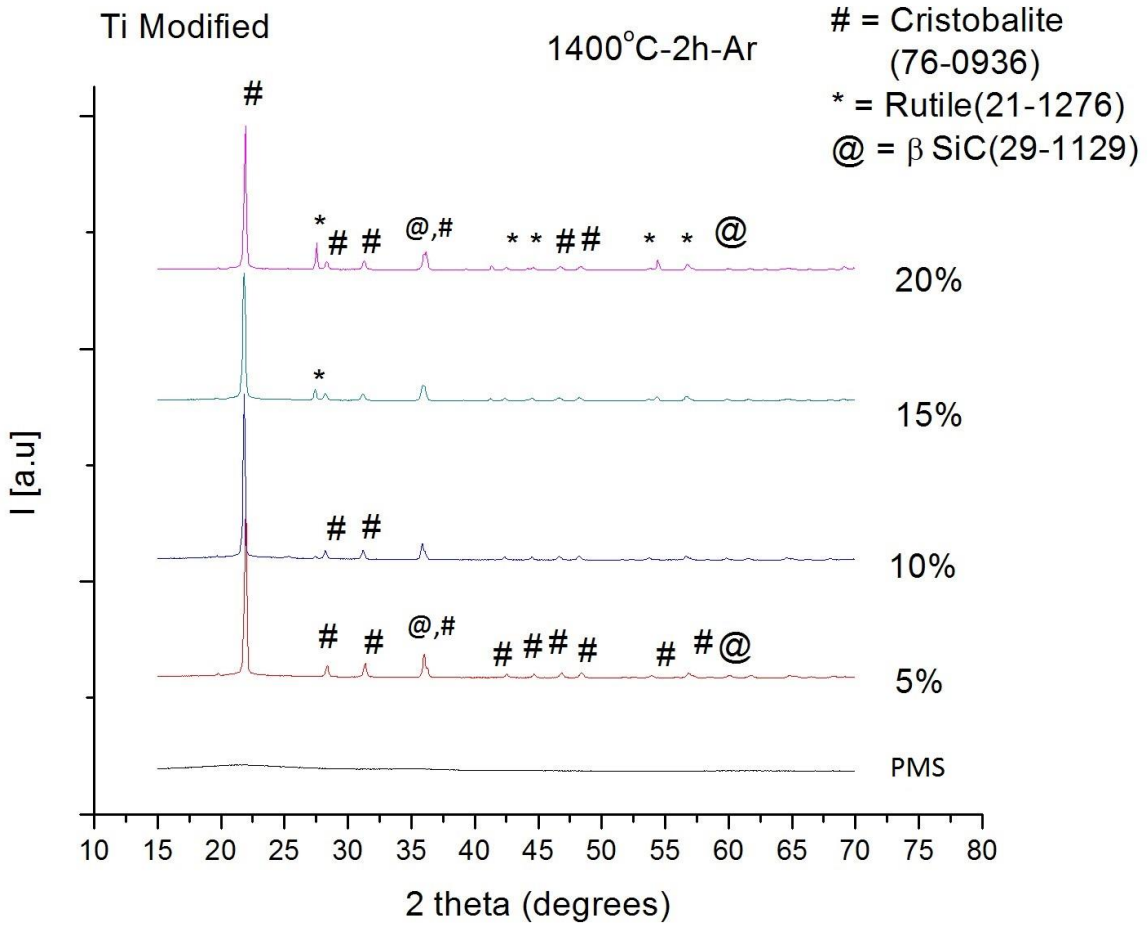


Figure 4.10: XRD analysis of different Ti- modified compositions pyrolyzed at 1400 °C

The XRD analysis of the Ti- modified silicon oxy-carbide pyrolyzed at 1400 °C is shown in the Figure 4.10. The undoped silicon oxy carbide shows amorphous nature even when pyrolyzed at 1400 °C. The 5% Ti- doped SiCO shows some no sign of titania formation as the 100% peak of titania which is generally present at 27.5° 2 theta value is absent in the graph. So a sharp peak of cristobalite is observed and at 36° 2 theta value there is a peak and a 60° peak confirms it to be β silicon carbide (29-1129) which can be examined in the standard file presented in figure 4.5 and 4.9. The same set of features are observed for 10% Ti- doped SiCO ceramics. As the doping

amount is increased to 15% the 100% peak of titania is visible. We can thus infer that titania formation has started in this doping amount and phase separation of the Ti content has occurred. Further increase in Ti- doping amount in the structure to 20% the rutile peak at 27.5° is clearly visible along with the formation of silicon carbide in the structure. The cristobalite peak is clearly visible in the figures which suggest there is formation of a matrix of cristobalite in which the titania grains are formed along with silicon carbide in the structure.

All the batches pyrolyzed @1500°C

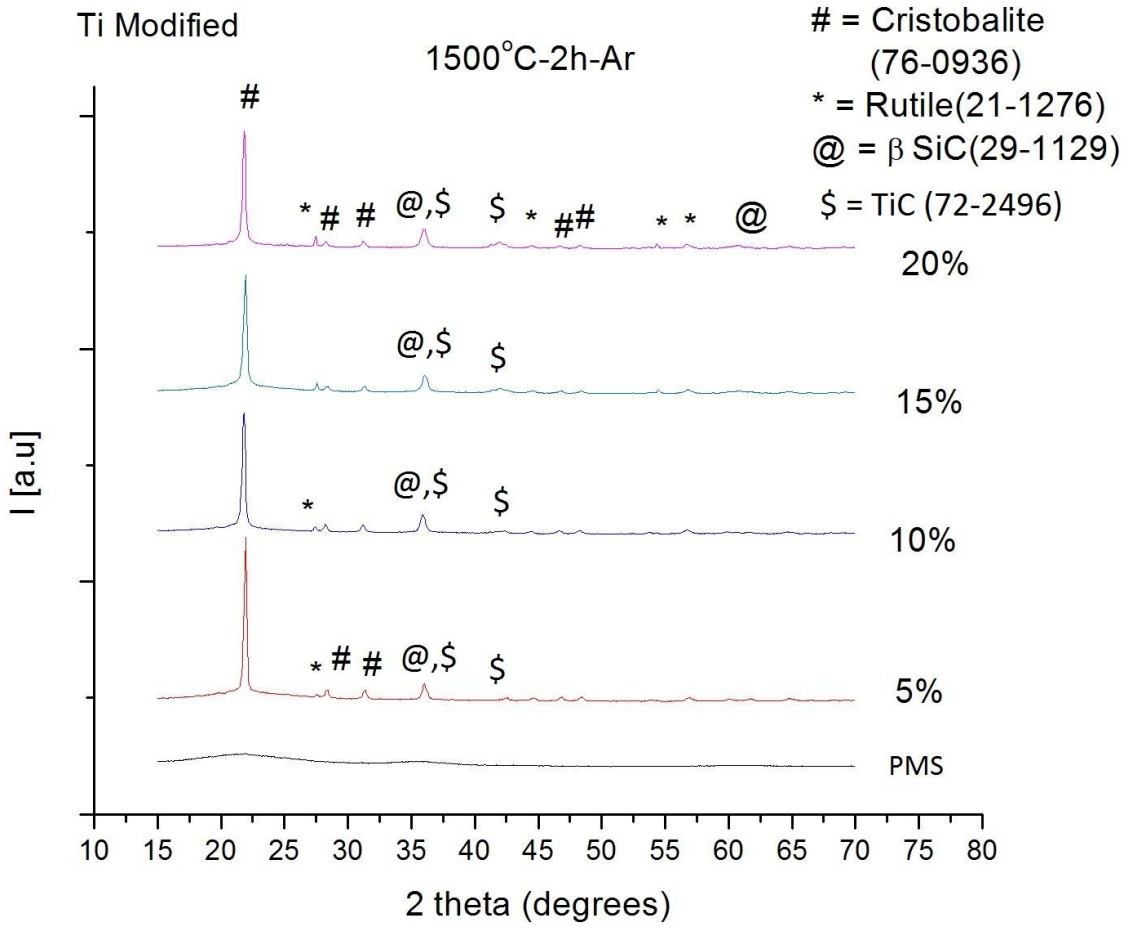


Figure 4.11: XRD Analysis of different Ti- Modified compositions pyrolyzed at 1500°C

As the pyrolysis temperature is further increased to 1500 °C the XRD analysis is shown in the figure 4.11. The following points can be concluded.

1. PMS derived SiCO at 1500 °C is amorphous in nature.
2. At 5% doped Ti, only peaks corresponding to SiO_2 cristobalite is observed. However unlike other low temperature results, the cristobalite peaks these materials seem very sharp and clearly positioned. There are clear peaks at about 36°, which corresponds to βSiC as analyzed in our

previous results. However, the peak at 36° appears to be slightly broad, and a combination of multiple peaks, on close observation.

3. The same features crop up for the 10% Ti doped sample with more clarity in addition to the peak at ~36°, a small peak at 60° - 61°. In combination with the facts it is proposed that there is concurrent formation of SiC as well as TiC.
4. For 15% Ti doped SiCO, TiO_2 (rutile) peaks emerge along with SiC and TiC, as discussed.
5. The 20% Ti doped ceramic appears to be a clearly crystalline ceramic with SiO_2, TiO_2 and TiC, SiC or the oxides and carbides of both the catio ns.

4.4 THERMAL BEHAVIOR OF MODIFIED SiOC

4.4.1 DSC-TG OF UNMODIFIED SiOC

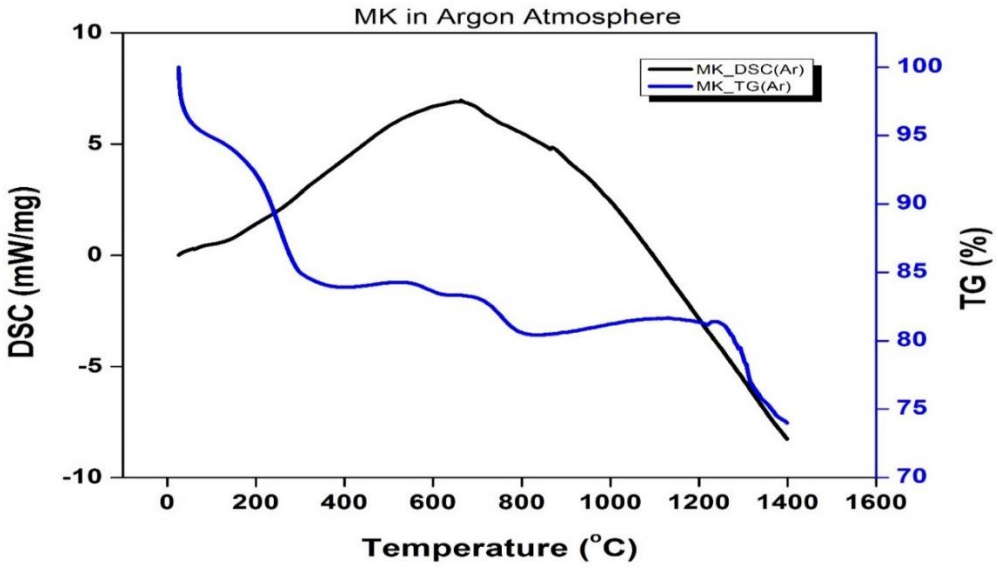


Figure 4.12 DSC-TG of PMS up to 1450°C in Argon atmosphere

4.4.1 DSC-TG OF Al MODIFIED SiOC

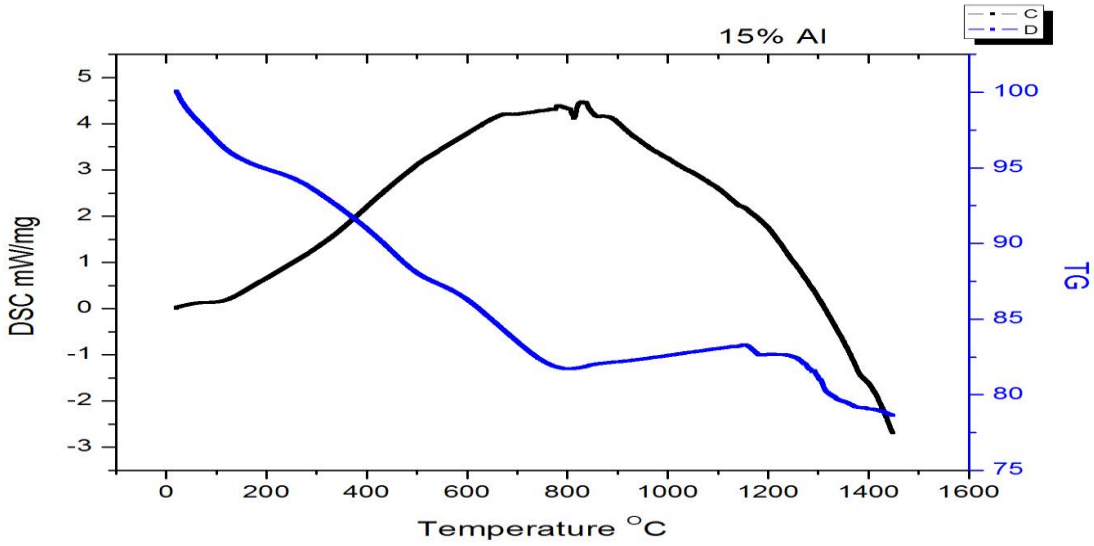


Figure 4.13 DSC-TG of 15AS up to 1450°C in Argon atmosphere

4.4.2 DSC-TG OF Ti MODIFIED SiOC

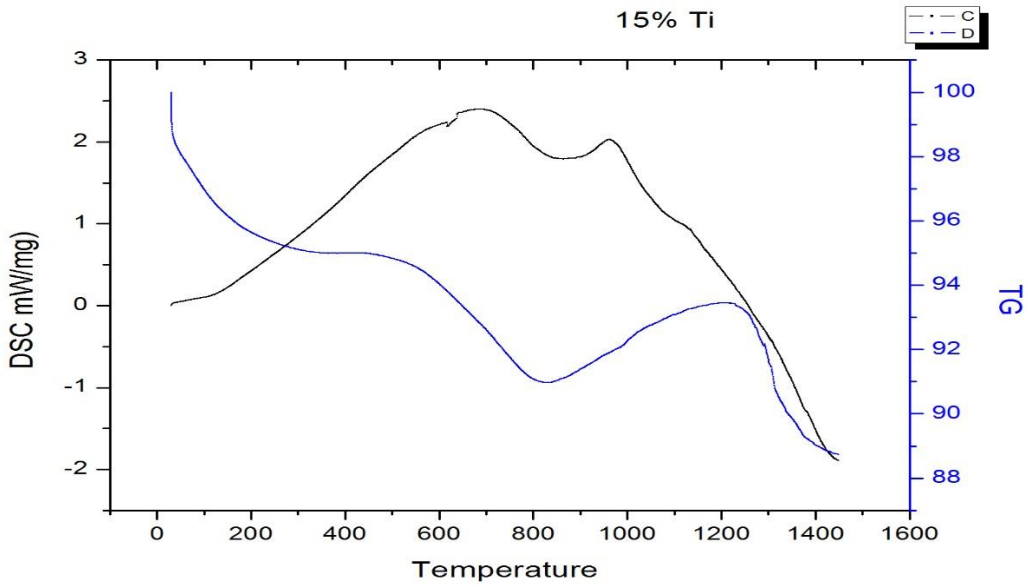


Figure 4.14 DSC-TG of 15TS in Argon atmosphere up to 1450 °C

Introduction of Ti in to the matrix also deceases the weight loss, which is evident from the figure 4.12. Up to 400 °C the weight loss is about 5% and corresponding DSC graph shows it to be exothermic. After 400 °C up to 800 °C there is another weight loss of 5% which is due to the decomposition of free C in the structure and evolution of gases out of the system. After 800 °C there is a gain in the weight which is 2 % this is due to the formation of TiO_2. .After 1200 °C there is a weight loss of 5% is observed. So a total of 11% weight loss is observed which is far more superior to undoped SiCO.

4.5 OXIDATION RESISTANCE BEH AVIOR OF SiCO

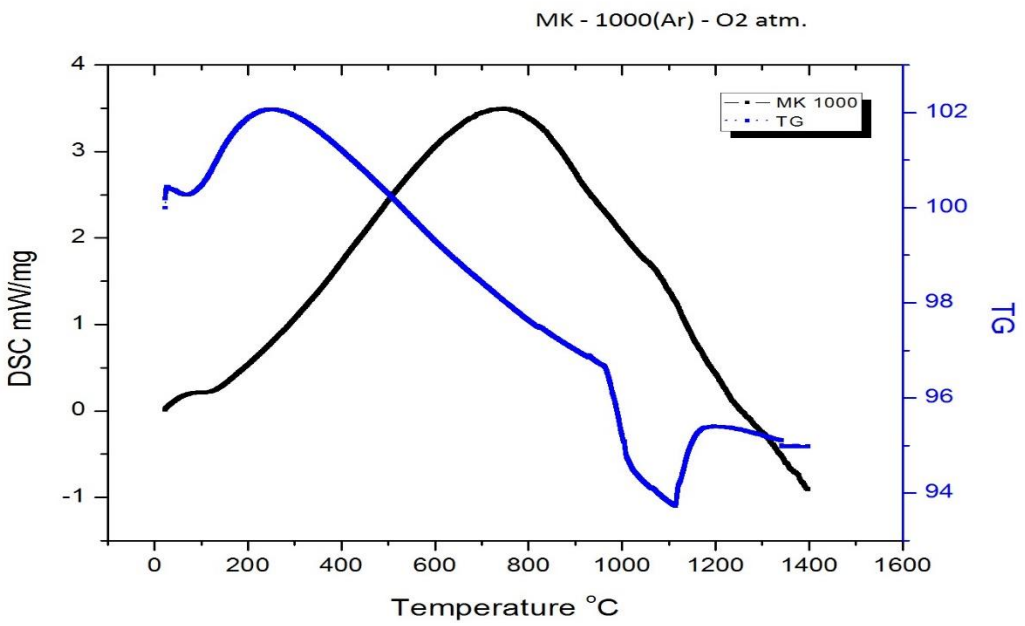


Figure 4.15 DSC-TG in oxygen atmosphere of MK pyrolyzed in Ar atmosphere up to 1450 °C

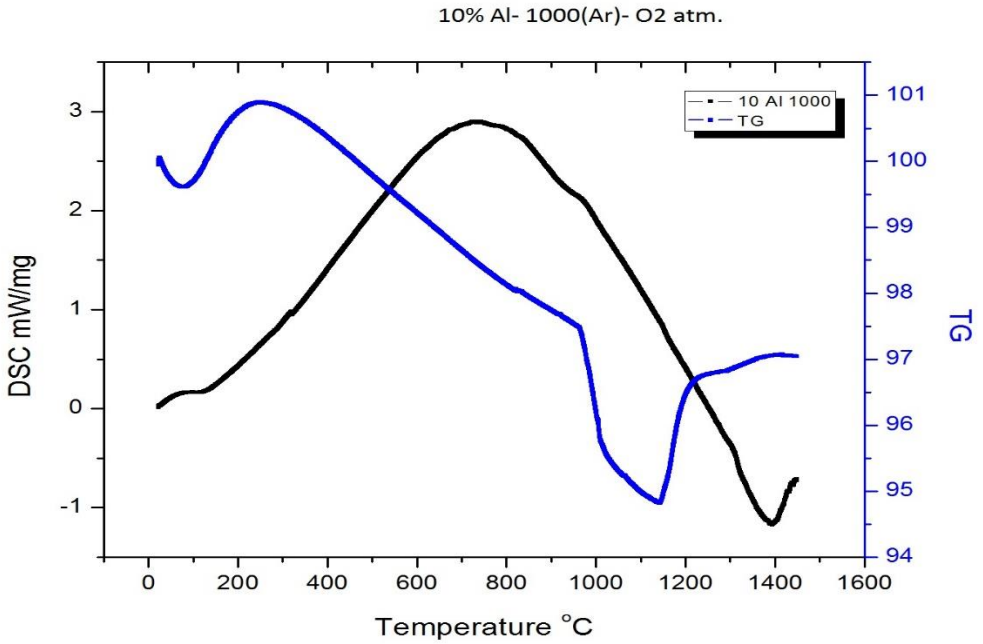


Figure 4.16 DSC-TG in oxygen atmosphere of 10AS pyrolyzed in Ar atmosphere up to 1450 °C

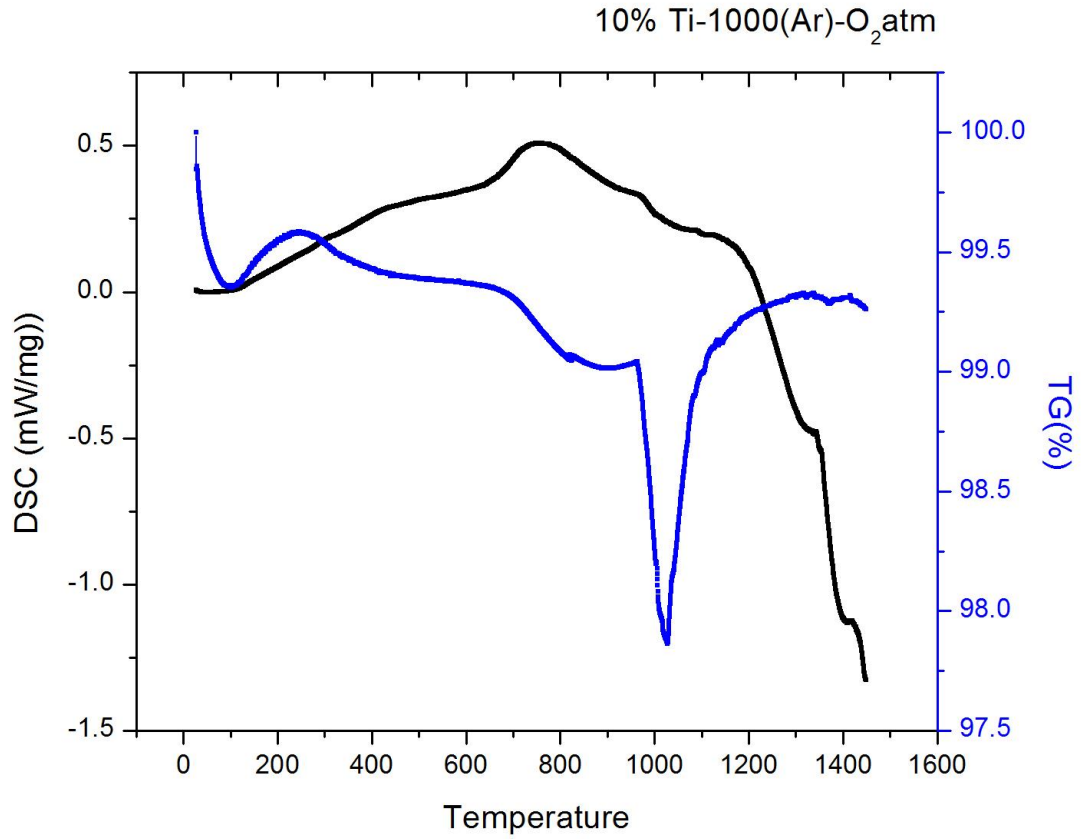


Figure 4.17 DSC-TG in oxygen atmosphere of 10TS pyrolyzed in Ar atmosphere up to 1450 °C

	RT-100	100-300	300-950	950-1100	1100-1450	Total Wt. Loss(%)
MK-1000(Ar)- O_2	-0.2	+2.2	-5.5	-2.7	+1.2	5
10% Al- 1000(Ar)- O_2	-0.5	+1.0	-4.0	-3.0	+2.5	4.5
10% Ti- 1000(Ar)- O_2	-0.75	+0.25	-0.5	-1.25	+1.5	1

Table 4.2 Weight loss at different region of pyrolyzed samples treated in O_2 atmosphere

The samples were pyrolyzed at 1000 °C in Ar atmosphere and then the oxidation was done up to 1450 °C. Pure poly methylsiloxane(PMS), 10% Al doped and 10% Ti doped samples were compared in terms of oxygen atmosphere thermal behavior. There were mainly 5 regions observed

to be prominent. The first region was between RT to 100 °C which shows the weight loss in the samples (amounts shown in the Table) which is due to the water loss. The second region is between 100 °C to 300 °C where there is a significant amount of weight gain the reason of which is not exactly determined. The third region is a loss region which spans between 300 °C and 950 °C which is due to the decomposition of free carbon in the structure. The fourth region is 950 °C to 1100 °C which is further loss region which can be related to the decomposition of the carbon which is partially free or strongly bonded to the structure. In the fifth region there is an abrupt weight gain in the samples after 1100 °C, which can be concluded as the further oxidation of the samples resulting in weight gain.

Chapter 6

CONCLUSION

Conclusion

- An attempt has been made to modify the silicon oxycarbide structure by incorporating transition metal element such as Al and Ti.
- Al was incorporated in the structure at the molecular level. Al was added in the increasing amount of mole percent (viz. 5%, 10%, and 15%) by using Aluminum iso-propoxide as Al source.
- All the samples were pyrolyzed at 1000 °C, 1200 °C, 1400 °C and the phase evolution was studied. Up to 10% doping can be accommodated in the glass structure without losing the amorphous nature of the samples till 1200 °C.
- Similarly, Ti was incorporated in the structure at the molecular level. Al was added in the increasing amount of mole percent (viz. 5%, 10%, 15%, and 20%) by using Titanium iso-propoxide as Ti source.
- All the samples were pyrolyzed at 1000 °C, 1200 °C, 1400 °C, 1500 °C and the phase evolution was studied. Up to 10% doping can be accommodated in the glass structure without losing the amorphous nature of the samples till 1200 °C.
- DSC-TG shows that the Al- doped PDC has almost same amount of weight loss after at high temperatures but the doping of Ti in the structure significantly reduces the weight loss. Thus it can be concluded the Ti goes in to the SiCO structure and replaces Si- but Al doesn't go in to the structure.

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